A STUDY OF THE POSSIBLE PRESENCE OF CARBOFURAN AND ITS METABOLITES IN GROUNDWATER

by

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SUMMARY

The n-methyl carbamate pesticide carbofuran (trade name Furadan) is being studied as an alternative to the banned DBCP as a post-plant nematocide in grape vineyards. Six shallow wells were sampled in selected rural areas of the San Joaquin Valley of California where carbofuran had previously been used. Selection criteria for the 6 areas sampled were: (1) identified previous treatments of the immediate area, (2) presence of a shallow well in the immediate area, and (3) presence of a sandy loam or loam soil. Each water sample was analyzed for carbofuran and 2 of its metabolites, 3-hydroxy carbofuran and 3-keto carbofuran. The results were negative for the 3 chemicals, each with a minimum detectable limit of less than 1 part per billion (ppb).

INTRODUCTION

Carbofuran is an n-methyl carbamate insecticide and nematocide that has been used in California for several years, mainly on rice and alfalfa. Like other n-methyl carbamates, carbofuran is a cholinesterase inhibitor. Rice accounted for almost 90 percent and alfalfa 8 percent of the amount of carbofuran reported used in 1980 in California. Use of the granular form of carbofuran in grape vineyards to control nematodes was registered under a Section 18 specific exemption in January of this year. Previous use of carbofuran on grapes had been done on an experimental permit.

Carbofuran is available in two formulations, flowable and granular. The flowable formulation is used on alfalfa at rates that range up to 1 lb. of active ingredient per acre. The granular formulation is being used in rice fields at 1/2 lb. of active ingredient per acre, and under the experimental uses and emergency exemptions in grape vineyards at 10 pounds of active ingredient per acre.

MATERIALS AND METHODS

This small survey included wells in the loam to loamy-sand soils of 5 San Joaquin Valley counties (San Joaquin, Stanislaus, Fresno, Tulare, and Kern). The selected wells were located in areas where carbofuran had previously been used on grape vineyards and alfalfa fields. Although applications of carbofuran on rice accounted for 90 percent of its use in 1980, the rice growing area (Sacramento Valley) was eliminated from testing considerations because the clay soils are not typical of grape-growing areas. Where the proposed new use at the significantly higher dose rates would occur, Furadan 4F (Reg. No. 279-2876-AA) was used on alfalfa, while both Furadan 4F and Furadan 10G (Reg. No. 279-2712-ZC) were used on the grape vineyards.

Each sample was collected from the stream of running water from the well after the pump had been operating at least 30 seconds. Quart-sized Mason jars were used to take the samples. The jars were filled, and aluminum foil was placed on top of the jar; then the lid was screwed down tight over it. An official sample seal was placed over the lid before the jar was placed on wet ice to be kept cool. Analysis of the samples was accomplished within 1 to 3 days of collection.

The method of analysis was by high pressure liquid chromatography (see Appendix 1). The analysis was run for the parent material and the metabolites 3-hydroxy carbofuran and 3-keto carbofuran, with the results given in Table 1. The minimum detectable limit was less than 1 ppb.

DISCUSSION AND CONCLUSION

Six water samples were drawn from wells in the immediate area where carbofuran was used. These wells were selected because the use history of carbofuran was known, the soil types were typical of grape-growing areas, and a shallow well was available in the immediate area for testing. The analysis showed no detectable residues of carbofuran and the 2 metabolites 3-hydroxy carbofuran and 3-keto carbofuran down to the minimum detectable limits of less than 1 ppb for each. The results of this sampling suggest that carbofuran is completely degradated before it leaches into the groundwater, if in fact its breakdown products reach groundwater in any detectable amounts.

APPENDIX 1

HPLC ANALYSIS OF CARBOFURAN AND ITS METABOLITES 3-HYDROXY CARBOFURAN AND 3-KETO CARBOFURAN FROM WATER

250g water sample was taken and extracted with three 50 ml portions of Methylene Chloride. The cumulated methylene chloride extract was evaporated to 3-5 ml using rotary evaporator at 50 degrees. Final evaporation to dryness was done under a slow current of air at room temperature. The volume was made to 3 ml in Acetonitrile and analyzed by HPLC.

HPLC CONDITIONS:

COLUMN: Altex Ultrasphere-ODS
4.G mm I.Dx 15 cm.
dp 5 micron

L.C. SOLVENTS:
Solution A: Acetonitrile + 10 drops of Phosphoric acid/L of ACN
Solution B: Water + 10 drops of Phosphoric acid/L of water.
RATE OF FLOW: 1.6 ml/min.
TYPE OF RUN: GRADIENT from 30% A to 70% A at the rate of 4% A/min. change.
AMOUNT SHOT: 20 microliter.

DETECTOR: Fluorescent
Solvent A: .05 N Sodium Hydroxide.
Solvent B (Reaction Solution): 0.05 g o-phthaldehyde and 1.0 ml 2-mercaptoethanol in 10 ml methanol is added to 50 ml Premix diluent and diluted to 1000 ml with water.
FLOW OF SOLVENT A: 0.5 ml/min.
FLOW OF SOLVENT B: 0.5 ml/min.
TEMP. OF REACTION FLASK: 100 degrees.

Range 3 PM gain: Low Response: Normal Mode: Normal
Excitation wave length 340 nm Slit width: 15 nm.
Emission wave length 455 nm Slit width: 12 nm.

The system was found to be linear from 4 ng to 18 ng of Carbofuran and its metabolites. Response beyond 18 ng was not checked as this was found to be suitable range for working.

RECOVERY: At 6 ppb level

Carbofuran	103%
3-Hydroxy Carbofuran	72%
3-Keto Carbofuran	101%

REACTION SOLUTION RESPONSE: 1.0 ml, 0.5 ml, 0.3 ml, and 0.15 ml of reaction solution was pumped in by keeping solution A constant at 0.5 ml/min. The detector response was lower at higher flow rate of reaction solution. 0.5 ml/min. or less flow rate was found to be suitable for maximum response.

REFERENCE: Krause, R.T.J.A.C.A.C. Vol. 63 No. 5, 1980 pg 1114.

TABLE 1

Results of Analysis of Water From Shallow Wells for Residues of Carbofuran and Two of Its Metabolites in Selected Areas of the San Joaquin Valley Where Carbofuran Had Previously Been Applied in the Immediate Area and the Soil Type Was Considered Conducive to Migration of Chemicals

Sample #	County	Material Used	Application		Area Treated	Crop Treated	Soil Type	Approximate Water Table Level	Well Depth	Results			Other Pertinent Data
			Dates	Rates (lbs. AI/A)						Carbofuran	3-hydroxy Carbofuran	3-keto Carbofuran	
1	San Joaquin	Furadan 10G	1/5/75	10 lbs.	<2 A	*Grapes - Carignane variety	loamy sand	72′	—	ND	ND	ND	The well's pump ran for about 3-1/2 hours before the sample was drawn. All applications were very close to the pump. The grape vineyards were flooded after each application
			4/1/76	10 lbs.	1/4 A								
			2/1/81	10 lbs.	2 A								
2	San Joaquin	Furadan 10G	12/2/74	10 lbs.	16 A	*Grapes - Zinfandel variety	sandy clay loam	18′	100′	ND	ND	ND	The vineyard treated in 1974 and 1975 was 1/4 mile away from the well. The other treated vineyards were 100 to 150 yards away from the well. The pump had not been used since the previous summer. The pump was run for about 1 minute before the sample was drawn. Water: PH = 5.4; CEC = 7.54; organic matter = 0.73%
			11/22/75	10 lbs.	8 A								
			12/4/75	10 lbs.	1-1/2 A								
		Furadan 10G & Furadan 4F	3/27/78 or 5/2/78	varied: 5-10 lbs.	12 rows by 72 rows								
		Furadan 10G	12/11/78	varied: 5-10 lbs.	8 rows by 24 rows								
		Furadan 10G	12/10/79	varied: 5-10 lbs.	8 rows by 24 rows								
3	Stanislaus	Furadan 4F	3/77	1/2 lb.	47 A	Alfalfa	sandy loam	8′	—	ND	ND	ND	Due to the high water table, water is pumped out of the ground continuously by drainage pumps. The sample was drawn from a drainage pump that was in the middle of the treated field.
			3/78	1/2 lb.									
			3/79	1/2 lb.									
			3/80	1/2 lb.									
4	Fresno	Furadan 4F	12/31/78, 18 dates in 1980 & 6 dates in 1981	Most of the applications were at 1 lb. Exceptions were at less than 1 lb.	less than 1/10 of an acre was involved each time (within an area of 3 acres)	Alfalfa	loam	50′	195′	ND	ND	ND	The well was about 70 yards from the treated field. The well had been used within the previous 2 weeks. The pump was run for about 2 minutes before the sample was drawn.
5	Tulare	Furadan 4F	3/78	3/8 lb.	120 A	Alfalfa	loam	90′	200′	ND	ND	ND	The well was at the edge of the field. The well had been used within the previous 2 weeks. The pump was run for about 30 seconds before the sample was drawn.
			3/79	3/8 lb.									
			3/80	1/4 lb.									
6	Kern	Furadan 4F	3/79	1/2 lb.	112 A	Alfalfa	sandy loam	100′	—	ND	ND	ND	The well was at the edge of the field. The well had been used within the previous 2 weeks. The pump was run for about 30 seconds before the sample was drawn.
			3/80	1/2 lb.									
			3/81	3/8 lb.									

*Treated under an experimental use permit.